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Report No. IITRI-C6014-13
(Triannual Report)

DEVELOPMENT OF SPACE-STABLE
THERMAL-CONTROL COATINGS
(PAINTS WITH LOW SOLAR ABSORPTANCE/
EMITTANCE RATIOS)

George C. Marshall Space Flight Center

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DEVELOPMENT OF SPACE-STABLE THERMAL-CONTROL COATINGS
(PAINTS WITH LOW SOLAR ABSORPTANCE/EMITTANCE RATIOS)

January 20, 1964 to June 20, 1964

Contract No. NAS8-5379
IITRI Project C6014

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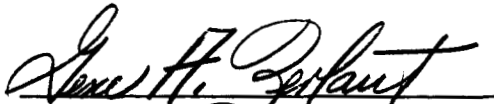
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FOREWORD

This is Report No. IITRI-C6014-13 (Triannual Report) of

IITRI Project C6014, Contract No. NAS8-5379, entitled "Investi-

gation of Environmental Effects on Coatings for Thermal Control

of Large Space Vehicles."   The report covers the period from

January 20 to June 20, 1964.   Previous Triannual Reports were

issued on October 25, 1963 and March 5, 1964.

Major contributors to the program included Gene A. Zerlaut,

Project Leader; Y. Harada and H. Rechter, inorganic coatings;

Edwin H. Tompkins and Richard C. Reichel, microporous structures;

Warren Jamison, space-chamber operation; Douglas G. Vance,

silicone paint preparation; and L. U. Berman, silicone photolysis.
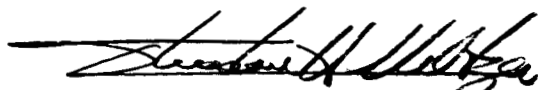
Data are recorded in IITRI Logbooks C13423, C13736, C13802,

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Respectfully submitted,
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ABSTRACT

DEVELOPMENT OF SPACE-STABLE THERMAL-CONTROL COATINGS
(PAINTS WITH LOW SOLAR ABSORPTANCE-EMITTANCE RATIOS)

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This report describes studies aimed at the development of stable thermal-control coatings with the lowest possible ratio of solar absorptance to infrared emittance. Included are discussions of microporous coating investigations, inorganic pigment and binder studies, methyl silicone paint studies, and a preliminary analysis of silicone photolysis reactions.

The principle problems associated with the use of foamed (microporous) polymer films are discussed in detail. Recent studies with a proprietary silicone blowing agent and with techniques involving the preparation of silicone resin emulsions have shown promise as methods of preparing microporous, foamed surface coatings. The most important aspects of the inorganic studies involved the improved reflectance and ultraviolet-vacuum stability realized by heat treating the pigments and the coatings made from them. The effect of grinding time (mill time) on the reflectance and stability of zinc oxide-silicone paints are discussed. It was found that long mill times cause increased solar absorptance and decreased stability of these paints. The effect of pigment particle size was investigated and experiments are discussed which involve mixing two zinc oxide pigments with widely different mean particle sizes.

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I.   INTRODUCTION

The goal of this research is the development of stable

thermal-control coatings with the lowest possible ratio of solar

absorptance to infrared emittance.   Earlier studies in this

program were in large part devoted to studies of techniques for

increasing the ultraviolet reflectance -- and therefore the solar

absorptance--of zinc oxide paints (both inorganic and silicone).

These studies were made in order to take advantage, if possible,

of the proven stability of the zinc oxide pigment system.

Early studies showed that in the use of secondary, ultra-

violet reflecting pigments, pigment mixing was generally unsuc-

cessful in improving the ultraviolet reflectance of zinc oxide

paints.   In addition, the technique of using overlayers of

ultraviolet-reflecting coatings on zinc oxide paints did not

have a great effect on the solar absorptance of zinc oxide coat-

ings.   The principal problem was attributed to the competition

between coatings thick enough to provide reflectance reinforce-

ment in the ultraviolet and coatings thin enough not to detract

significantly from longer wavelength reflectance and the ultra-

violet/vacuum stability of the system.

Work during this report period has generally involved three

phases, namely, (1) studies of microporous structures, (2) studies

of pigments and inorganic silicate paints, and (3) studies of methyl silicone paints. Although these studies are essentially a continuation of the work begun at the start of the program, increased emphasis has been placed on pigment and inorganic vehicle screening, on the use of a commercial methyl silicone elastomer in the microporous structures investigations, and on the photolysis of methyl silicone polymers.

II. DEVELOPMENT OF MICROPOROUS STRUCTURE IN PAINT VEHICLES

A. Introduction

The current primary objective of this phase of the program is to prepare approximately 1μ bubbles at a high concentration in any vehicle of high ultraviolet stability. Because of the lack of other binders sufficiently stable to ultraviolet radiation in vacuum, the methyl silicone polymer system (polydimethylsiloxane) has received the most attention. Potassium silicate has also been considered as a vehicle for the suspension of micropores.

From the list of techniques discussed in the literature and in previous reports on the preparation of bubble structures, we have investigated the following three methods: (1) leaching of salt or starch from a polymerized dispersion in a silicone or other vehicle, (2) generation of gas from nitrogen blowing agents dispersed in methyl silicone vehicles, and (3) mechanical incorporation of air bubbles in methyl silicone polymers.

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The feasibility of reflecting the bulk of the solar spectrum with foamed, porous polymer structures was shown in the previous Triannual Report.[1] Commercial foams with exceptional reflectance in the 0.3 to 2.0μ wavelength region are available. Unfortunately, these foams are manufactured from polymers which are inherently unstable to ultraviolet radiation in vacuum--polyvinyl chloride, polyurethanes, and polystyrene. The methyl silicone polymer system has been found to be the most stable

$$\underset{CH_3}{\overset{CH_3}{Si}}-O\left(\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{\overset{|}{O}}{\overset{CH_3}{Si}}-O\right)_n\underset{CH_3}{\overset{CH_3}{Si}}-O$$
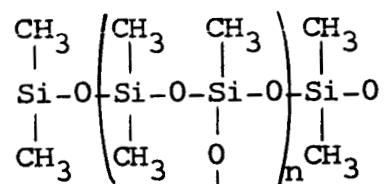
polymer species available in terms of ultraviolet irradiation in vacuum.[2] It has therefore been necessary to concentrate our laboratory studies on techniques to prepare polydimethylsiloxane foams and microporous structures.

The principal problem in foaming the methyl silicones has involved the control of pore size. The lack of control over pore size and concentration has been attributed to various factors, including (1) inability to incorporate sufficiently fine particles of blowing agent in the silicones, (2) lack of mutual solubility between blowing agents and the methyl silicones,

[1] G. A. Zerlaut, E. H. Tompkins, and Y. Harada, "Development of Space-Stable Thermal-Control Coatings," Triannual Report, IIT Research Institute, Report No. IITRI-C6014-8, March 5, 1964.

[2] G. A. Zerlaut and Y. Harada, "Stable White Coatings," Summary Report, IIT Research Institute, Report No. IITRI-C207-25, August 27, 1963.

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(3) inability to match the curing/rheological properties of the methyl silicones with the thermodynamic properties of the blowing agents, and (4) inability to satisfactorily leach soluble materials out of the relatively closed-pore silicone matrix.

Hundreds of bench formulations have been prepared during the course of this program, and only those experiments which were most typical have been reported to date. Accordingly, the following paragraphs discuss the more important work performed during the last reporting period.

B. Leaching

Three types of coatings have been considered for leaching experiments: (1) our standard zinc oxide-potassium silicate coatings, which have demonstrated unusual stability in space simulation tests, (2) zinc oxide-silicone films cast on glass plates with water-soluble release agents, and (3) ammonium chloride-silicone coatings.

Leaching of the zinc oxide from the coatings is performed with a 5M ammonium hydroxide aqueous solution containing ammonium chloride at a concentration of 1M. This solution attacks the air-dried zinc oxide-silicate quite rapidly and dissolves the zinc oxide. The overall reflectance decreases visibly, but the reflectance in the ultraviolet between 3250 and 4100 A, where the zinc oxide absorbs strongly, is increased from about 4 to 87% in the leached coating. The effect of leaching on the re-

flectance of a standard SP 500 zinc oxide-pigmented PS7 potassium silicate paint is shown in Figure 1.

The loss in reflectance in the bulk of the spectrum is attributed to the decrease in the ratio of the refractive index of the pigment (whether it be the zinc oxide particle or the pore) when the zinc oxide is leached, leaving a pore of approximately the same size. We do not know to what extent the potassium silicate is being dissolved, but if a significant portion of the silicate binder is being leached in the process, the system would show considerably more ultraviolet absorption. The main difficulty with this system is maintaining satisfactory film integrity after the zinc oxide has been removed. The utilization of this system would also require thicker films in order to minimize the decrease in reflectance at longer wavelengths. Alkali silicate coatings usually exhibit inferior mechanical properties when applied in thick films.

Studies on the leaching of ammonium chloride and zinc oxide from methyl silicone polymer films have been concerned primarily with methods of opening up of the pores in the silicone film. Earlier leaching studies on silicones involved the loading of General Electric's SR-80 silicone resin with sodium chloride and the subsequent leaching of the salt with water. This work, reported in the previous Triannual Report,[1] resulted in superficial leaching due to the closed-pore, hydrophobic silicone
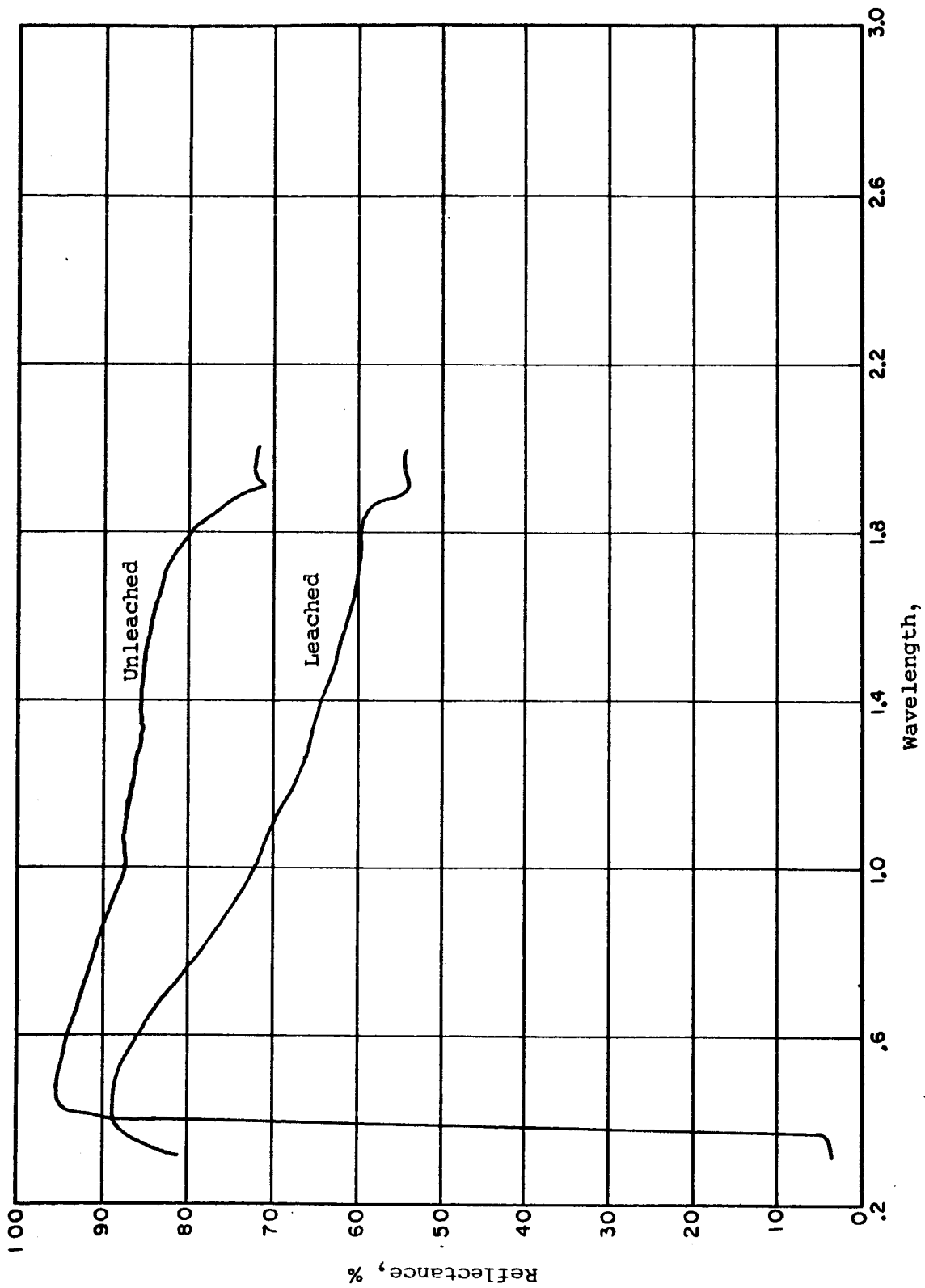
Figure 1

EFFECT OF LEACHING ON ZINC OXIDE-SILICATE COATING

matrix. We have tried a number of solvents (acetone, methyl ethyl ketone, methanol, and others) for the superficial removal of the polymer from a General Electric LTV-602 film containing 70% zinc oxide by weight. One film treated with tolune was subsequently leached with the ammonium hydroxide-ammonium chloride aqueous solution, but the leached film still showed strong zinc oxide absorption in the ultraviolet region of the reflectance spectrum. The primary clue as to whether or not leaching is being accomplished (removal of zinc oxide from the upper layers of the coating) is an increase in the ultraviolet reflectance of the coating. This has not yet been accomplished with the LTV-602 silicone vehicle.

The leaching of ammonium chloride from silicone coatings presents the same problems as zinc oxide leaching, except that ammonium chloride can also be sublimed out of the coating. Techniques learned from the zinc oxide studies will be applied to ammonium chloride leaching. Also, techniques for precipitating unusually fine ammonium chloride particles from aqueous solutions will be tried, including precipitation with hydrochloric acid and alcohol if a method can be worked out to successfully open the methyl silicone pores.

C. Blowing and Foaming Agents

Although over 1000 chemical blowing agents are known to the foamed plastics industry, only about 12 to 16 are commercially

feasible. Table 1 lists those that have received our attention for use in silicone polymers; most of these agents have been discussed in the two earlier Triannual Reports. Experiments have indicated that the Porofor N (azobisisobutyronitrile) is one of most satisfactory blowing agents for use in methyl silicone and aqueous potassium silicate solutions. The main difficulty in using Porofor N in potassium silicate solutions has been the inability to obtain a fine dispersion of the blowing agent in the vehicle. We have concentrated on mechanical dispersion without the use of surface active agents which are all expected to be ultraviolet degradable.

A special effort was made to obtain the blowing agent Porofor N in an extremely fine state for use in potassium silicate (and methyl silicone) vehicles. Results with comparatively coarse blowing agents in potassium silicate looked primising. We have accordingly tried precipitating the Porofor N out of methylene chloride solution by adding pentane (in which Porofor N is insoluble), but the precipitation is too slow for small-particle generation. Precipitation of Porofor N from ethyl ether with hexane is also too slow.

Rapid evaporation of the methylene chloride solution with added pentane yields relatively fine particles which were tried in potassium silicate. This method is not satisfactory for bulk preparation, but enough material was obtained to indicate

Table 1

CHEMICAL BLOWING AGENTS

Chemical Name	Structure	Trade Name	Decomp. Range in Plastics, °C	Gas Yield, cc/g (STP)	Remarks
Azodicarbonamide	$H_2N-CO-N=N-CO-NH_2$	Celogen AZ	160 - 200	225	Residue colorless and odorless. Original color is yellow.
Azobisisobutyronitrile	CH_3 CH_3 $NC-C-N=N-C-CN$ CH_3 CH_3	Porofor N	105 - 120	115	Residue colorless, toxic.
Dinitrosopentamethylene tetramine	CH_2-N-CH_2 $ON-N$ CH_2 $N=NO$ CH_2-N-CH_2	Unicel N	130 - 190		Residue colorless. Amine odor (hexamethylene tetramine). 60% silica filler.
Diazoaminobenzene	$C_6H_5 N=N-N-C_6H_5$	Porofor DB Unicel	100 - 130	130	Has phenyl groups and brown color. Residue staining and toxic.
4,4'-Oxybis(benzene-sulfonyl hydrazide)	H_2NNHO_2S-○-O-○-SO_2NHNH_2	Celogen OT	120 - 130	225	Residue colorless and odorless. OT refers to oil treated.
N,N'-Dimethyl-N,N'-dinitroso-terephthalamide	$H_3C-N-OC$-○-$CO-N-CH_3$ NO NO	Nitrosan	90 - 105	310	Residue colorless. Residue is dimethyl terephthalate.
Ammonium carbonate	$(NH_4)_2CO_3$		58		
Benzenesulfonyl-hydrazide	$C_6H_5SO_2-NHNH_2$	Porofor BSH	95 - 100		Colorless and odorless residue.
Ammonium nitrite	NH_4NO_2		70		

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that the bubble size of the blown silicate was still too large.

We have recently been concentrating on General Electric's proprietary LTV-602 methyl silicone potting compound, which forms clear elastomer films on curing. Various procedures have been tried in attempts to balance the curing properties with the gas-generation properties of the blowing agents. In this respect, various curing agents have been evaluated including SRC-04 and SRC-05 (proprietary catalysts for LTV-602) and metal soaps such as tin octoate, Thermolite 12, etc. Of the catalysts studied, tin octoate (Nuocure 28) produces the fastest cure in LTV-602 silicone.

General Electric's proprietary silicone blowing agent, RTV-921, has been obtained and preliminary experiments have shown promise. A foam was produced with LTV-602 by using the following formula:

> LTV-602 silicone polymer   10.0 g
> RTV-921 blowing agent   2.5 g
> Nuocure 28 (tin octoate)   14   drops

Foaming occured before the resin had set sufficiently, and, as a result, the upper half of the sample thickness contained foam bubbles and the lower half was bubble-free. Subsequent experiments in which the catalyst concentration (Nuocure 28) was varied showed that the milky appearance increased as the catalyst concentration increased.

Further experiments have been conducted to investigate the in-phase resin curing and foam generation. That is, the polymer

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formation, or cure, should be sufficiently progressed to enable retention of the generated foam. LTV-602 was catalyzed and allowed to stand for various time periods before the RTV-921 blowing agent was added. The effect of short periods of time at 200°F before the addition of the blowing agent was studied. These precedures resulted in specimens which were foamed throughout, although the bubbles formed were not of a uniform size and were, in general, much too large. The finest bubble size was obtained with a sample that gelled during mixing. Its formula is given below:

No. 5:   LTV-602 silicone polymer   12 g
                Nuocure 28 (tin octoate)   6 drops
                RTV-921 blowing agent   2.5 g

        The LTV-602 and Nuocure 28 were mixed
        and placed in a 200°F oven for 5 min.
        Gelation started after 5 min. at 200°F.
        The RTV-921 blowing agent was added
        (mixed with difficulty). The system
        gelled after mixing about 1 minute.

Another sample of interest has the following formula:

No. 1   LTV-602 silicone polymer   10 g
                Nuocure 28 (tin octoate)   5 drops
                RTV-921 blowing agent   2.5 g

        The LTV-602 and Nuocure 28 were mixed
        and allowed to stand for 70 min. before
        adding RTV-921 blowing agent. The mix-
        ture was quite thick and very tacky.
        The blowing agent addition seemed to has-
        ten the final set. The mixture was placed
        in a 200°F. oven. It set in 10 min. with
        slight expansion.

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Sample no. 1 had a fairly good foam, but was not as white as sample no. 5. The reflectance of 250-mil thick specimens of nos. 1 and 5 are presented in Figure 2. Examination of this figure indicates that the bubbles are too large, and visual examination shows insufficient concentration and a considerable number of very large bubbles which allow deep penetration of the light. The influence of the silicone spectra, which is considerably more pronounced than anticipated, is shown in Figure 2. The complexity of the bands and indeed several of the bands themselves, have not been observed even as weak bands in the pigmented systems.

D.   Mechanical Incorporation of Bubbles

Since some commercial methods of foam manufacture involve the mechanical introduction of bubbles, we have evaluated this method as a means of producing microporous coatings. Mechanical incorporation of air bubbles in potassium silicate vehicles has been tried with a standard Waring blender. The viscosity of the silicate solution was allowed to vary over a wide range during evaporation of the water solvent, but no useful foams were obtained. Similar experiments with silicones verify, as expected, that mechanical aeration techniques would have to be studied extensively before useful results could be obtained. Surface-active agents have not been used in these studies because of their instability to ultraviolet radiation.
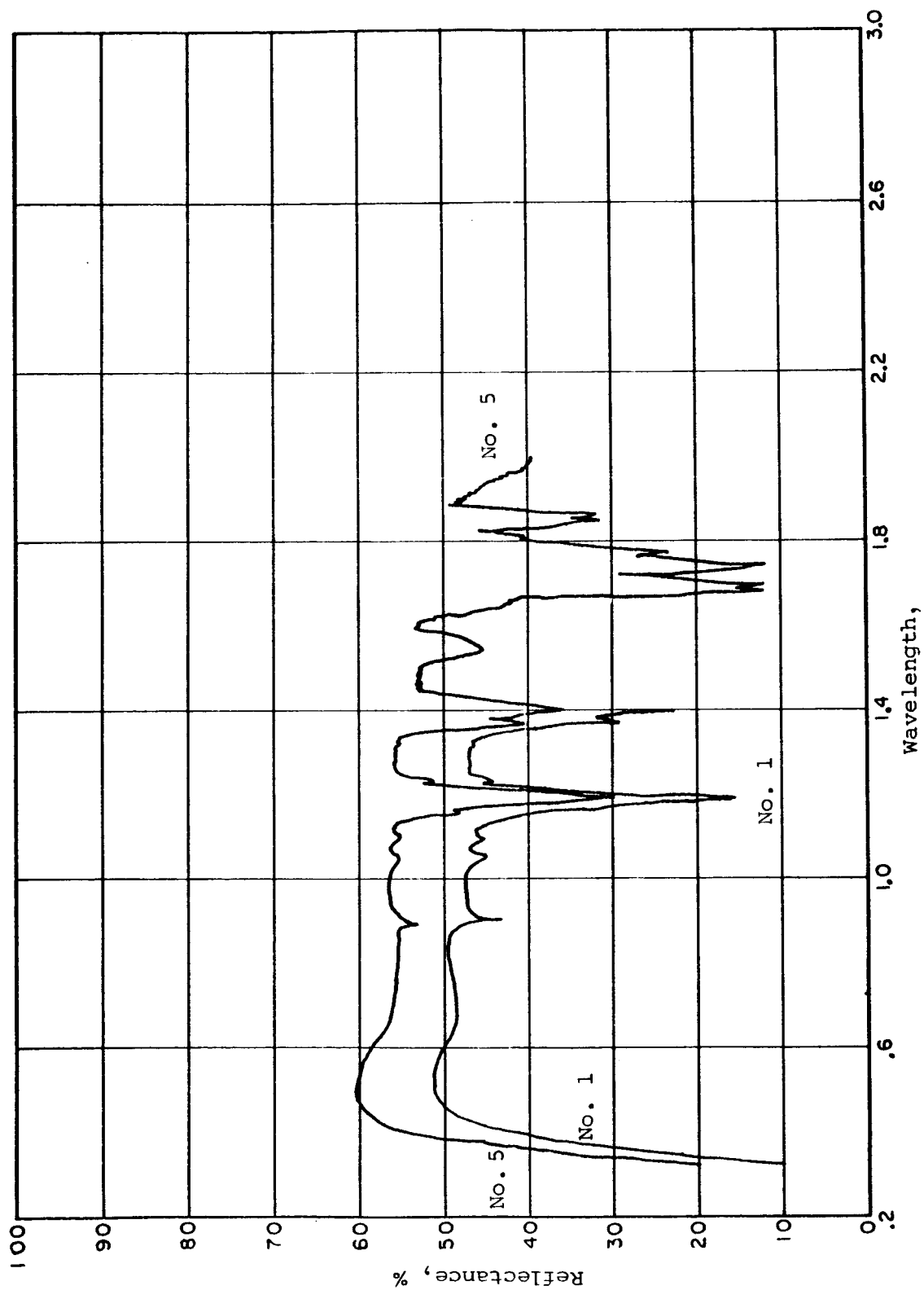
Figure 2

REFLECTANCE OF LTV-602 FOAMED COATINGS

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We have, however, found that aqueous potassium silicate yields a surprisingly white coating by itself in the form of a thick film when dried at 180°F for several hours. Under a microscope the whiteness appears to be due to separated crystals. This process appears to be a variation of the polymer segregation mechanism discussed in a previous report. In potassium silicate, the whiteness might be enhanced at an intermediate stage of curing by a methanol treatment. We are considering this and other variations.

E. Other Methods of Incorporating Porosity

The use of emulsion techniques has recently appeared promising as a method of producing porosity in LTV-602 films. A water emulsion was prepared by using morpholene and oleic acid; the first sample had approximately 60% water. The slow addition of water makes an ever-increasing paste with the silicone resin. This paste is very white. After a certain point is reached, at approximately 35% water, the paste begins to thin with the continued addition of water. If the addition of water is stopped at the point where the thickest paste is obtained, a film can be obtained which appears to have a very fine particle size when viewed under the microscope. Although the LTV-602 does not solidify as usual, the paste does harden on loss of water (which occurs slowly), leaving a rather coarse bubble structure.

F.   Summary and Future Plans

One fact increasingly evident in the silicone work is that wider variations in the chemical and mechanical properties of these polymers would greatly facilitate the generation of micro-porous structures.   As pointed out, the difficulty in breaking the closed-pore silicones, the difficulty in matching the curing and rheological properties of the methyl silicones with the gas forming properties of the blowing agents, and the lack of mutual solvents for the resins and blowing agents have all served to hinder the development of desirable microporous coatings.   However, because of the potential of this concept for maximizing the reflection of solar radiation, we plan to continue this investigation.

The use of other commercial methyl silicones, when available, are contemplated.   The use of silicone fluid (oil) diluents in conjunction with the SRC-05 catalyst in order to prepare better LTV-602 foams with the RTV-921 blowing agent will be considered. Such diluents are used in preparation of General Electric's RTV-60 silicone rubber foams.   In addition, three new blowing agents have been obtained from E. I. du Pont, and they will be evaluated in the near future.   Other emulsifying agents will be evaluated in conjunction with the emulsification of LTV-602 and other silicone polymers.   Our studies of techniques to break the closed pores will be continued in an effort to perfect

a satisfactory method of leaching soluble materials from methyl silicone films.

II.   INORGANIC COATINGS

A.   Introduction

The work during this report period has been concerned with obtaining systems with high reflectance and good resistance to an ultraviolet-vacuum environment.   This has involved a continued investigation of hitherto unstudied pigments and also an examination of the effects of temperature on both optical properties and stability.   The beneficial results of improved reflectance and ultraviolet-vacuum stability realized by heat treatments are the most significant aspects of the recent work.

B.   Pigments

In the continuing search for potential pigments, a number of materials were gathered and examined optically in the range 0.325 to 2.0μ by utilizing the Cary Spectrophotometer.   The various materials were calcined to determine the effect of heat treatment on reflectance.   Values at representative wavelengths are presented in Table 2.

All materials studied showed enhanced reflectance in the infrared to varying degrees.   In the visible and ultraviolet portions of the spectrum, improved reflectance was relatively minor and was not realized for all materials.   Petalite, Kona F-4 and Edgar ASP revealed the most significant increases.   The

Table 2

EFFECT OF HEAT TREATMENT ON REFLECTANCES OF VARIOUS MATERIALS

Sample No.	Material	Heat Treatment	% Reflectance* at microns										
			0.325	0.375	0.450	0.600	0.700	1.0	1.2	1.4	1.6	1.8	2.0
4	Lithafrax	None	90.5	93.5	92.5	92.5	91.5	90.0	91.0	91.0	91.5	91.5	92.5
4-C	(Lithium Aluminum Silicate)	800°C/6 hr	89.0	92.0	91.5	92.5	91.5	90.0	91.5	93.5	92.0	92.5	95.0
5	White Barytes	None	76.5	83.0	89.0	91.5	91.5	90.0	90.5	91.0	91.0	91.0	90.0
5-C	(Barium Sulfate)	800°C/6 hr	78.0	82.0	85.5	90.5	90.0	89.5	91.0	93.0	92.0	92.5	95.0
6	Kona-F-4	None	75.0	79.5	82.5	86.0	86.0	85.5	87.0	88.5	88.5	88.5	89.5
6-C	(Potassium Aluminum Silicate)	800°C/6 hr	74.5	80.0	83.5	91.0	91.0	91.5	93.0	94.5	93.5	94.0	96.0
11	Nepheline Syenite	None	83.0	86.0	87.5	88.0	87.0	85.5	85.5	86.0	86.5	87.0	87.0
11-C	(Sodium Potassium Aluminum Silicate)	800°C/6 hr	79.0	82.5	83.5	88.5	88.0	88.5	89.5	92.0	91.0	91.5	94.0
12	Talc	None	71.0	80.0	82.0	85.0	84.5	80.0	83.0	77.0	83.0	82.0	75.0
12-C	(Magnesium Silicate Hydrate)	800°C/6 hr	45.5	63.0	71.5	74.0	72.0	82.0	86.5	89.0	90.0	90.0	90.5
14	Petalite	None	76.5	81.5	83.5	84.5	83.5	81.5	81.5	80.0	81.0	81.0	80.0
14-C	(Lithium Aluminum Silicate)	800°C/6 hr	81.0	85.0	85.0	88.0	87.0	86.0	87.5	89.0	88.0	88.0	90.0
2	Potassium Metaphosphate	None	85.5	96.0	95.5	95.0	94.5	92.0	92.5	92.0	90.0	85.5	80.5
2-C		500°C/16 hr	81.0	96.0	96.0	95.5	93.5	90.5	90.5	92.0	91.0	91.0	91.0
15	Spinel	None	91.5	94.5	93.5	93.0	91.0	86.5	85.5	79.5	78.0	72.0	62.0
15-C	Magnesium Aluminate	500°C/16 hr	93.5	97.0	96.0	95.0	93.0	89.0	87.5	83.5	82.5	79.5	71.0
17	Edgar 4SP	None	31.0	61.0	76.0	85.0	86.0	87.0	86.0	59.0	84.5	75.0	67.5
17-C	Aluminum Silicate	800°C/16 hr	32.0	72.5	86.0	91.0	91.0	90.5	90.5	90.5	90.0	88.0	83.0
18	Superpax	None	64.0	77.5	84.5	88.5	88.0	87.0	86.5	86.0	86.0	84.0	82.5
18-C	Zirconium Silicate	800°C/16 hr	63.0	78.5	86.5	90.5	90.0	88.5	89.0	89.0	90.0	88.5	89.0

*Based on magnesium oxide.

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approach to enstatite through partial loss of water of talc (900°C is the water-loss temperature) colored the material significantly. These experiments indicate a method by which optical properties of a pigment can be altered. Another method by which materials can be whitened is acid washing. Removal of colored contaminants in zircon has been accomplished in this manner.

The higher reflectance and hence, lower solar absorptance, realized through heat treatment might be accompanied by other desirable effects. For the extremely fine, fluffy powders, agglomeration and possible particle size increase will permit the use of less diluent in paint formulation thus yielding improved physical properties. Earlier work[1] with zinc oxide powders has also shown that improved resistance to ultraviolet-vacuum can be obtained by calcination. Although no similar beneficial effect from heat treatment was observed for alumina, zirconia, and zircon, [1] the possible volatilization of contaminants and elimination of defects suggest that calcination could be a standard procedure for pigments.

C. Paints

1. Ultraviolet-Reflecting Topcoats

A space-simulation experiment was conducted to determine the stability of a zinc oxide-silicate system coated with a thin layer of silicate-bonded zirconia. Figure 3 illustrates the

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complete experimental sample measuring 1 x 3 in. and the 1 X

1/2 in. test specimens (Nos. 1 to 4) which were cut from the

parent.   Samples 1 and 3 were heated at 400°C for 2 hrs.

Samples 2 and 4 received no treatment.   Previous experiments

have shown the beneficial effect of heat on the stability of

zinc oxide-silicate coatings.   Data for this experiment, con-

ducted at a solar factor of 11.0 suns and a pressure of less

than 10^{-7} torr, are tabulated in Table 3.
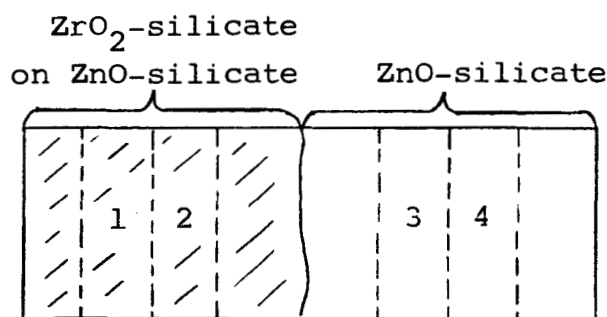
Figure 3

EXPERIMENTAL SAMPLE AND CUT SPECIMENS

A comparison of original values, i.e., before irradiation,

of samples 2 and 4 reveals the improvement in reflectance of

the topcoated specimens.   Upon heat treatment, the reflectance

of zirconia (No. 1) decreased, but that of zinc oxide (No. 3)

did not.   The solar absorptance changes due to topcoating are

concentrated in the α_1 region of the spectrum (ultraviolet and

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Table 3

EFFECT OF ULTRAVIOLET IRRADIATION IN VACUUM ON
ZIRCONIA-SILICATE TOPCOATED ZINC OXIDE-SILICATE SYSTEM
TEST V44

Sample	Exposure, ESH*	Solar Absorptance			
		α_1	α_2	α	$\Delta\alpha$
1	0	0.088	0.085	0.172	
	2560	0.130	0.081	0.211	0.039
2	0	0.068	0.081	0.149	
	2560	0.163	0.087	0.251	0.102
3	0	0.101	0.076	0.176	
	2560	0.107	0.070	0.178	0.002
4	0	0.102	0.080	0.182	
	2560	0.122	0.073	0.194	0.012
5-19-6**	0	0.080	0.120	0.200	
	2560	0.141	0.110	0.251	0.051

*ESH = equivalent sun-hours.

*Silicate-bonded zirconia coating.

visible). Comparison of α_2 values of the dual systems with those of 5-19-6 shows the superior infrared reflectance of the former.

Irradiation in the space chamber resulted in significant degradation of the topcoated samples. The heat-treated sample, however, was considerably more stable than the air-dried sample. A curious result was the inferior stability of the composite (Sample 2) in comparison to that of the pure zirconia coating.

2. Effect of Heat on Reflectance

The beneficial effect of a heat treatment of 500°C on stability to ultraviolet irradiation in vacuum has been shown for both zinc oxide-[1] and zirconia-pigmented films. However, the solar absorptance for zinc oxide was lowered and the solar absorptance for zirconia was raised.

Coatings of these two materials were examined by utilizing the Cary Spectrophotometer before and after a 500°C treatment. Spectral curves appear in Figure 4. The zirconia film was applied on a Pyrex substrate, and the zinc oxide coating was applied on abraded aluminum. Both samples showed significant improvement in the infrared region; apparently the heat treatment results in volatilization of water and thus elimination of the water absorption band, which exists at about 2μ.

In the visible portion of the spectrum, the reflectance of zinc oxide increased and the reflectance of zirconia decreased
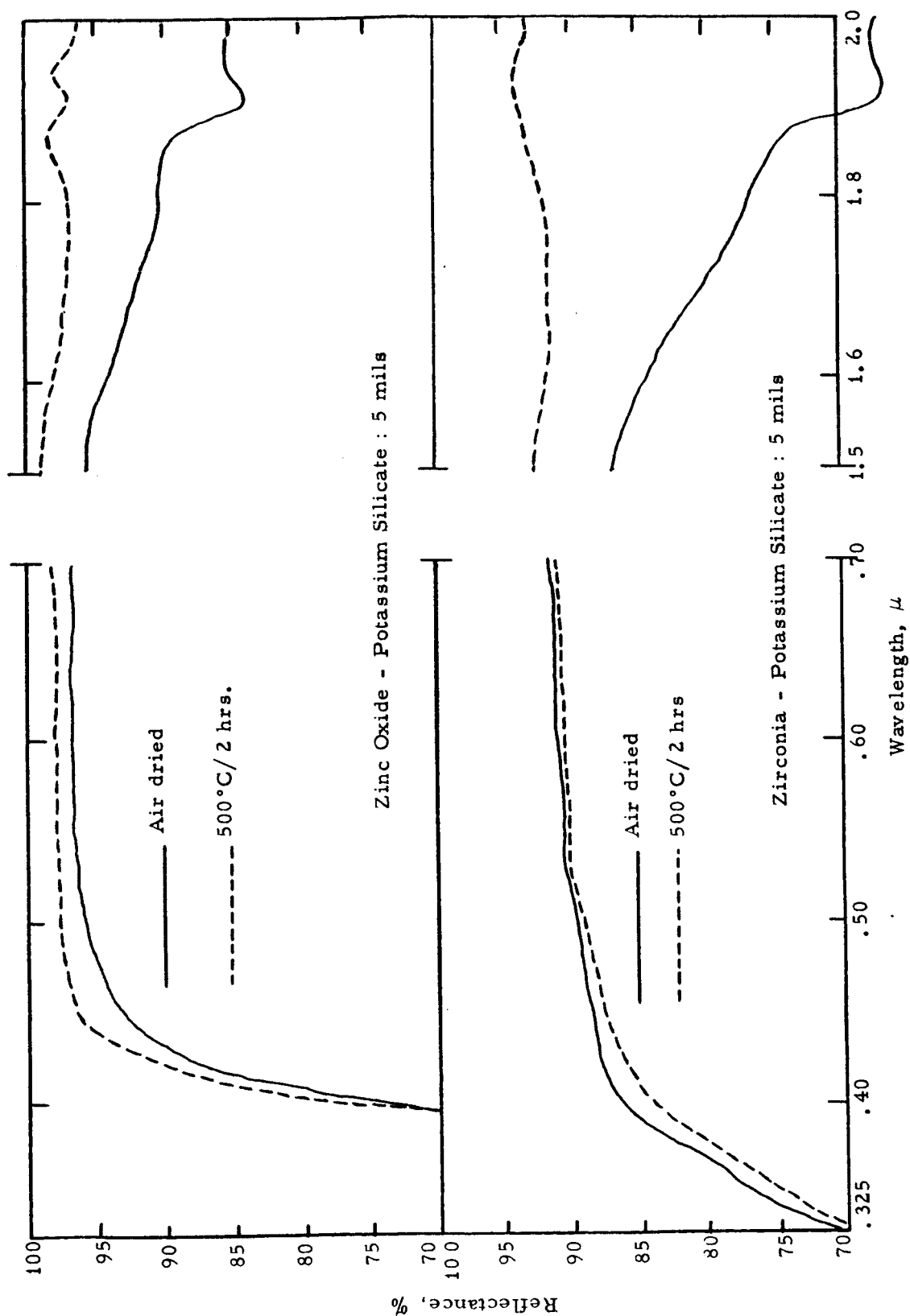
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EFFECT OF HEAT TREATMENT ON REFLECTANCE OF ZnO AND ZrO$_2$ COATINGS

Figure 4

-- both to a limited degree. Although not shown, a zirconia
coating on abraded aluminum suffered a stronger reflectance
loss in the visible than the Pyrex-backed sample; the reflectance
increase in the infrared region did not appear to be substrate-
dependent.

Heat-treatment experiments were also conducted with diato-
maceous earth-pigmented silicate coatings. Figure 5 contains
spectral curves for thin coatings heated to two temperatures.
Elimination of the 2μ water band is again apparent in these
coatings. However, the high-fired sample revealed a reflectance
loss throughout the wavelength region examined. With thicker
coatings (Figure 6), the 500°C as well as the 150°C treatment
improved reflectance.

These experiments suggested that reflectance losses result-
ing from a 500°C firing were partially due to the lower reflect-
ance of the aluminum substrate when oxidized. A 150°C treatment
of a zirconia-silicate coating affected only the infrared portion
of the spectrum; an increase was observed. Further calcination
at 500°C resulted in a decreased reflectance in the visible and
additional increase in the infrared. A thin, 2-mil zinc oxide-
silicate film heat-treated at 500°C revealed a reflectance drop
in the visible which has not been observed with thicker coatings.

The observed improved reflectance in the infrared for sili-
cate bonded cotaings with heat treatment is not an irreversible
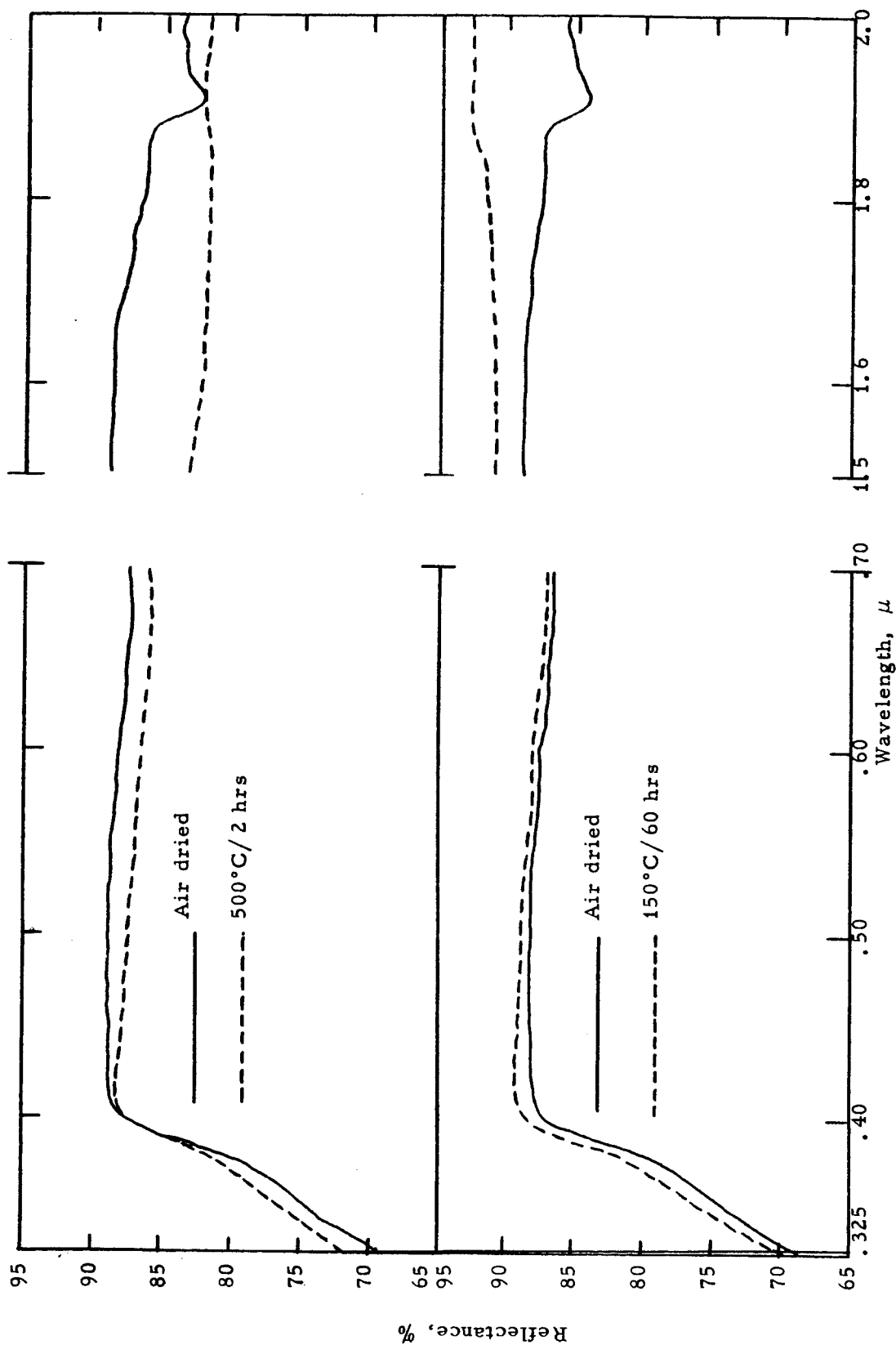
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Figure 5

EFFECT OF HEAT TREATMENT ON REFLECTANCE OF THIN (4 mil) SILICATE–BONDED
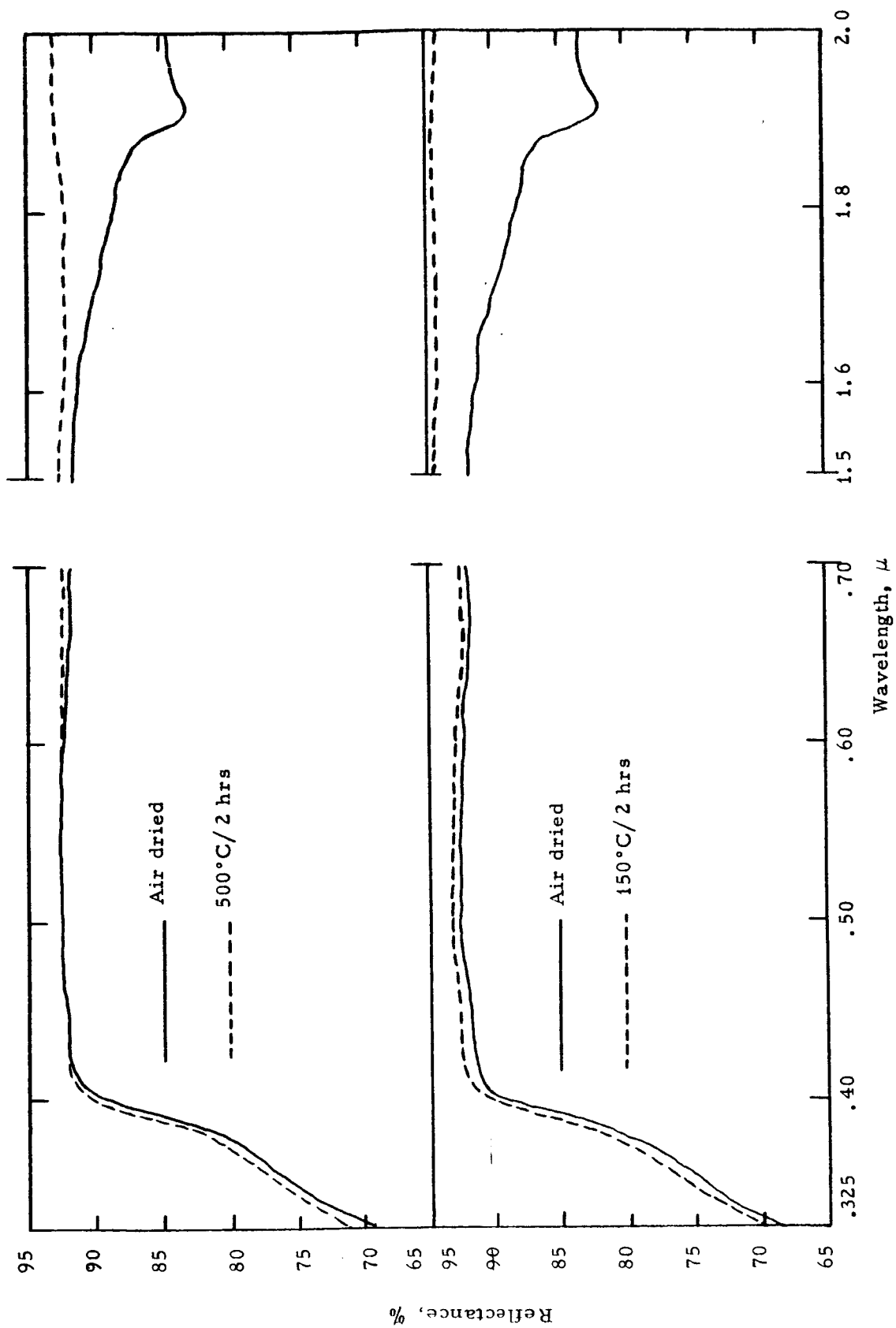DIATOMACEOUS EARTH COATINGS

Figure 6

EFFECT OF HEAT TREATMENT ON REFLECTANCE OF THICK (8 mil) SILICATE-BONDED
DIATOMACEOUS EARTH COATINGS

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phenomenon. Optical examination of heat-treated samples after periods of time shows that the infrared curve drops slightly with time, indicating a reintroduction of the water absorption band at about 2μ. However, this is a relatively slow process; lapses of 50, 33, and 8 days for 500°C heated diatomaceous earth, zinc oxide, and zirconia coatings, respectively, did not result in a complete decrease in reflectance from the infrared back to the original. It is possible that factors other than water loss contribute to infrared reflectance increase upon heat treatment.

Improvement in reflectance in the infrared region results not only from water loss but probably from a change in the optical characteristics of the silicate matrix. Potassium silicate air dries to a clear film; opacification of the film occurs at temperatures >100°C.

Experiments were also conducted to determine the optical effects of topcoating a silicate-bonded zinc oxide coating with a vehicle alone. Curing of such a system at 150°C produced a slight improvement in ultraviolet reflectance up to about 18% and marked deterioration in the infrared region beyond 1.6μ. Heating at 500°C raised the ultraviolet reflectance to 70 to 80% and also enhanced infrared reflectance. However, the overall curve from 0.325 to 2.0μ was significantly lower than that for the highly reflecting zinc oxide-silicate substrate.

3.   Effect of Heat Treatment on Resistance to Ultraviolet-Vacuum

A series of space-simulation experiments was conducted to examine the effects of heat treatment on the stability of silicate-bonded coatings.   The parameters for the tests were as follows:

Test No.	V47	V51	V52
Exposure (ESH)*	2005	2010	1015
Solar Factor	10.7	6.9	11.7
Pressure	maintained at less than 10^{-7} torr.		

*equivalent sun hours.

Samples of silicate-bonded diatomaceous earth and zirconia were subjected to ultraviolet irradiation in vacuum for 2000 ESH in Test 47.   Heat-treated samples as well as air-dried coatings were examined in this experiment.   The results are given in Table 4.

The beneficial effect of the 500°C treatment on stability is obvious for both compositions and is stronger for the zirconia sample.   A 150°C treatment did not appear to change the degradation characteristics for diatomaceous earth; similar observations have been made with both zinc oxide and zirconia coatings in past work.   In all cases a bleaching effect in the infrared portion of the spectrum resulted from space simulation.   For the diatomaceous earth samples, the crossover, i.e., the intersection of the unirradiated and irradiated reflectance curves,

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Table 4

EFFECT OF ULTRAVIOLET IRRADIATION IN VACUUM ON
SILICATE-BONDED DIATOMACEOUS EARTH AND ZIRCONIA COATINGS
TEST V47

Sample	Pigment	Heat Treatment	Exposure, ESH	Solar Absorptance			
				α_1	α_2	α	$\Delta\alpha$
H-13-14	Diatomaceous earth	None	0	0.075	0.097	0.172	
			2000	0.131	0.098	0.229	0.057
H-13-16	Diatomaceous earth	150°C/66 hr	0	0.075	0.094	0.170	
			2000	0.133	0.095	0.228	0.058
H-13-15	Diatomaceous earth	500°C/2 hr	0	0.072	0.090	0.163	
			2000	0.108	0.093	0.200	0.037
1-9-12	Zirconia	None	0	0.066	0.106	0.172	
			2000	0.141	0.106	0.247	0.075
1-9-13	Zirconia	500°C/2 hr	0	0.081	0.102	0.183	
			2000	0.110	0.100	0.210	0.027

Note: Binder for all samples was PS7 potassium silicate. Diatomaceous earth samples had a pigment-to-binder ratio of 2.15 and the zirconia samples, 4.30.

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occurred at about 1.7μ, and for the zirconia, at about 1.4μ. This penomenon did not radically manifest itself in a gain in α_2, since the bleaching effect, which affects only about 20 and 30% of the α_2 solar energy spectrum for the two systems, was balanced by a degradation in the wavelength region 0.7 to 1.4 and 1.7μ.

Test V51 was conducted to determine the effect of the substrate material, if any, on the beneficial effect of heat treatment on stability. Also included in this experiment were two paints incorporating Lithafrax (lithium aluminum silicate). Sample WL-5 was prepared over a year ago, whereas No. 1-20-79 was of very recent vintage. The results are tabulated in Table 5.

The similar behavior of zirconia coatings applied on aluminum and on Pyrex showed that the substrate material does not play a role on the resistance of heated coatings to ultraviolet-vacuum. The rather high initial solar absorptance values for the Lithafrax coatings were somewhat surprising; Lockheed has been able to obtain an α for this composition as low as 0.13.[3] Either application techniques or the use of a more reflective lithium aluminum silicate obtained by processing is responsible

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[3]R. L. Olson, L. A. McKellar, and J. V. Steward, "The Effects of Ultraviolet Radiation on Low $\alpha s/\epsilon$ Surfaces", Preprints, Symposium on Thermal Radiation of Solids, Session IV, San Francisco, California, March 5, 1964.

Table 5

EFFECT OF ULTRAVIOLET IRRADIATION IN VACUUM ON
SILICATE-BONDED ZIRCONIA AND LITHAFRAX COATINGS
TEST V51

Sample	Pigment	Comments	Exposure, ESH	Solar Absorptance			
--------	---------	----------	---------------	α_1	α_2	α	$\Delta\alpha$
1-9-3	ZrO_2	On aluminum	0	0.067	0.111	0.178	
			2010	0.115	0.117	0.232	0.054
1-9-4	ZrO_2	On aluminum, 500°C/2 hr	0	0.078	0.103	0.180	
			2010	0.103	0.103	0.206	0.026
1-9-P2	ZrO_2	On Pyrex, 500°C/2 hr	0	0.077	0.103	0.180	
			2010	0.105	0.101	0.206	0.026
WL-5	Lithafrax	Prepared in May, 1963	0	0.084	0.128	0.212	
			2010	0.150	0.121	0.271	0.059
1-20-79	Lithafrax	Prepared in May, 1964	0	0.076	0.116	0.192	
			2010	0.119	0.108	0.227	0.035

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for their lower values. The superior stability for the fresher sample, No. 1-20-79, suggests possible contamination or aging of the one-year-old sample.

Test V52 involved a series of calcined zirconia coatings for determining the temperature required for improved stability. Solar absorptance measurements were made before and after calcination as well as after space simulation; the results are presented in Table 6. There is a strong possibility that the indicated temperature is 50 to 100°C high. A thermocouple probe analysis showed a fairly wide temperature gradient in the furnace.

A lowering of initial α was realized at lower heat treatments, and an increase resulted at the higher temperatures. Heat-treatment effects on stability exhibited a curious peak at the lower temperatures; mild heating produced a more degradable coating. Improvement in ultraviolet-vacuum resistance became apparent at 400 and 500°C. Also included in this experiment was a pigment sample of zirconia. Much stronger degradation occurred for this pigment than for the silicate-bonded paints, indicating a protective effect for the vehicle.

Paints incorporating calcined potassium metaphosphate were also exposed in Test V52. This pigment has a refractive index fairly close to that of the silicate binder; thicknesses greater than 10 mils were required for good opacity. Although potassium metaphosphate is highly reflective, incorporation of this material

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Table 6

EFFECT OF ULTRAVIOLET IRRADIATION IN VACUUM
ON PIGMENTS AND SILICATE-BONDED COATINGS
TEST V52

Sample	Pigment	Comments	Exposure, ESH	Solar Absorptance			
				α_1	α_2	α	$\Delta\alpha$
1-9-9	Zirconia	Air-dried	0	0.066	0.109	0.175	
			1016	0.162	0.103	0.265	0.090
1-9-10	Zirconia	Air-dried, 200°C/2 hr	0	0.067	0.108	0.175	
			0	0.068	0.103	0.171	
			1016	0.177	0.114	0.291	0.120
1-9-11	Zirconia	Air-dried, 300°C/2 hr	0	0.067	0.107	0.174	
			0	0.064	0.102	0.166	
			1016	0.174	0.112	0.286	0.120
1-9-14	Zirconia	Air-dried, 400°C/2 hr	0	0.066	0.110	0.176	
			0	0.075	0.108	0.183	
			1016	0.168	0.113	0.280	0.097
1-9-15	Zirconia	Air-dried, 500°C/2 hr	0	0.068	0.110	0.177	
			0	0.075	0.106	0.182	
			1016	0.140	0.109	0.249	0.067
H-15-28	Potassium Metaphosphate	Air-dried, 300°C/2 hr	0	0.062	0.112	0.174	
			0	0.080	0.128	0.208	
			1016	0.144	0.139	0.283	0.075
H-15-29	Potassium Metaphosphate	Air-dried	0	0.058	0.110	0.168	
			1016	0.159	0.116	0.275	0.107
Pigments: #43	Zirconia		0	0.041	0.056	0.097	
			1016	0.181	0.072	0.253	0.156
#45	Zinc Titanate	700°C/4 hr	0	0.062	0.056	0.118	
			1016	0.091	0.060	0.150	0.032

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into a silicate-bonded coating yielded relatively high α's.
Calcination at 300°C produced a significant loss in reflectance.
Some improvement in stability was realized by the heat treatment.

Promising stability was exhibited by the zinc titanate, an
experimental material furnished by the New Jersey Zinc Research
Laboratories. Its solar absorptance is also lower than that of
zinc oxide (about 0.13). Paints incorporating this material
have been prepared and will be examined optically and subjected
to space simulation. Other samples of zinc titanate containing
excess TiO_2 or ZnO are also on hand and will be studied.

IV. METHYL SILICONE COATINGS

A. Effect of Grind Time on Reflectance and Stability

Recent 2000-ESH exposures of S-13 (SP 500 zinc oxide-pig-
mented LTV-602) specimens which were milled in a 5-gal. porelain
ball mill resulted in solar absorptance increases, Δα's, of from
0.06 to 0.08. These values were considerably higher than had been
observed previously for laboratory-size preparations (½ pint).
This anomaly prompted investigations which are summarized in
Table 7. Examination of the data in Table 7 shows that the
Δα, or ultraviolet stability, is a function of the length of
grind of the zinc oxide paints. This appears to be true both
for small capacity mills as well as for the large 5 gal. mill.
A graphical presentation of the data is shown in Figure 7, which
indicates that stability is achieved after rather short grind

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Table 7

EFFECT OF SPACE SIMULATION ON S-13 PAINT
GROUND FOR DIFFERENT LENGTHS OF TIME

Mill Capacity	Grind Time, hr	Exposure, ESH	Solar Absorptance			
			α_1	α_2	α	$\triangle\alpha$
1 qt*	0	0	0.096	0.097	0.193	
		2560	0.113	0.109	0.222	0.029
1 qt	1	0	0.098	0.099	0.197	
		2560	0.108	0.117	0.225	0.028
1 qt	3	0	0.098	0.098	0.196	
		2560	0.109	0.109	0.217	0.021
1 qt	30	0	0.118	0.107	0.225	
		2560	0.199	0.115	0.314	0.089
5 gal**	1	0	0.101	0.119	0.220	
		2000	0.120	0.141	0.261	0.041
5 gal	2	0	0.116	0.142	0.258	
		2000	0.124	0.151	0.275	0.017
5 gal	3	0	0.105	0.126	0.231	
		2000	0.118	0.144	0.262	0.031
5 gal	5	0	0.095	0.104	0.199	
		2000	0.123	0.135	0.258	0.059

*1/2-in. diameter x 3/4 in. cylinders.

**3/4-in.-diameter balls.

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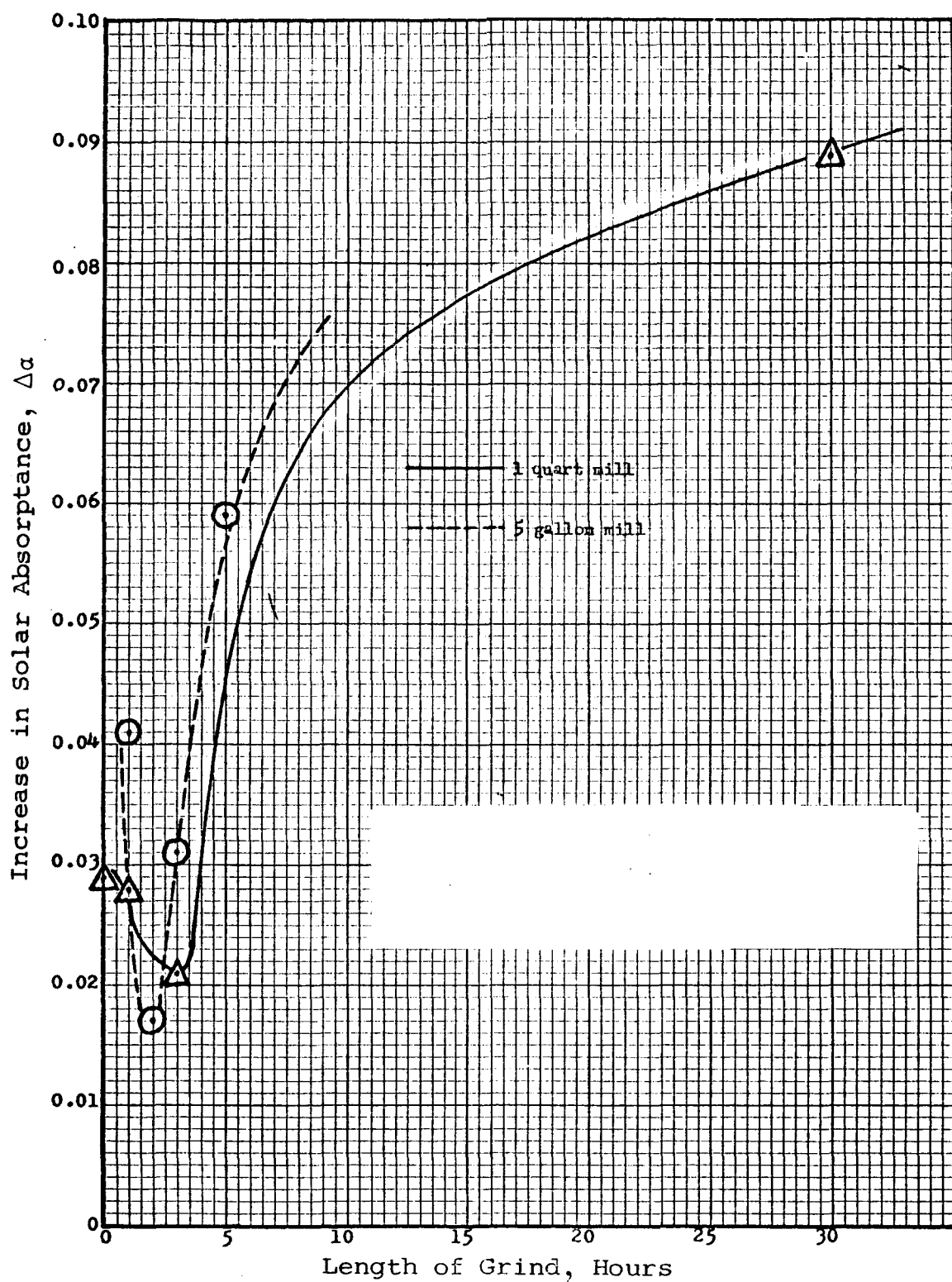IITRI-C6014-13

Figure 7

EFFECT OF LENGTH OF GRIND ON UV-STABILITY OF
S-13 (2000-ESH EXPOSURE)

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times of only 2 to 3 hrs., regardless of the size mill used.

The shape of the curves presented in Figure 7 is explained as follows: the initial increase in stability (decrease in effect on solar absorptance) is attributed to an increased degree of dispersion of the pigment. That is, the initially high $\Delta\alpha$ is probably due to photolysis of islands of polymer which are unprotected by the screening effects of zinc oxide. The minima is thought to occur when the beneficial nature of improved dispersion no longer counterbalances the degrading influence of the length of grind. The latter is thought to be due either to silica contamination as a result of the shearing forces which occur during the pigment grind (which become significant at longer grinds) or at the high shear rates which might be encountered in the large mills with heavy ball charges.

Other time-dependent factors have not been discounted, however. Chief among these is the known shearing effect of lattice distortion which occurs in zinc oxides. This results in a shift in the observed reflectance minimum (edge) to longer wavelengths with an accompanying yellowness. This is in turn manifested in the increased α_1 which is observed in the 30 hr. grind specimen. It should be noted that the 5 hr. grind specimen was prepared at a considerably greater thickness than the other specimens prepared in the 5-gal. mill. Thus, the trend cannot be inferred from that set of data. The specimens

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prepared in the 1-quart mill, however, were all prepared at 5-mil film thicknesses. The fact that the initial solar absorptance (before exposure) is lowest (i.e., highest solar reflectance) is attributed to the optical effect of the lattice distortion. Therefore, a simple experiment will be performed to test whether the observed decrease in stability (higher $\Delta\alpha$) with length of grind is due to silica contamination or to an inherent decrease in the stability of zinc oxide as a result of lattice distortion. A quantity of zinc oxide will be distorted by either grinding in an agate mortar and pestle or compacting at high pressures and will then be milled in the S-13 formulation for 2 to 3 hrs. A large increase in solar absorptance on ultraviolet irradiation in vacuum will indicate that the primary cause of instability is lattice distortion rather than silica contamination. If this experiment is inconclusive, chemical analysis will be utilized to determine the presence, if any, of silica or other contamination.

B.   Effect of Calcination of Zinc Oxide

The effect of calcination of SP 500 zinc oxide on the reflectance of the basic S-13 paint (LTV-602) is presented in Figure 8. The pigment was calcined for 16 hrs. at 640°C and then incorporated into the S-13 formulation. The solar absorptance of the basic S-13 formulation is 0.22 and that of the paint formulated from the calcined pigment was 0.18. These data
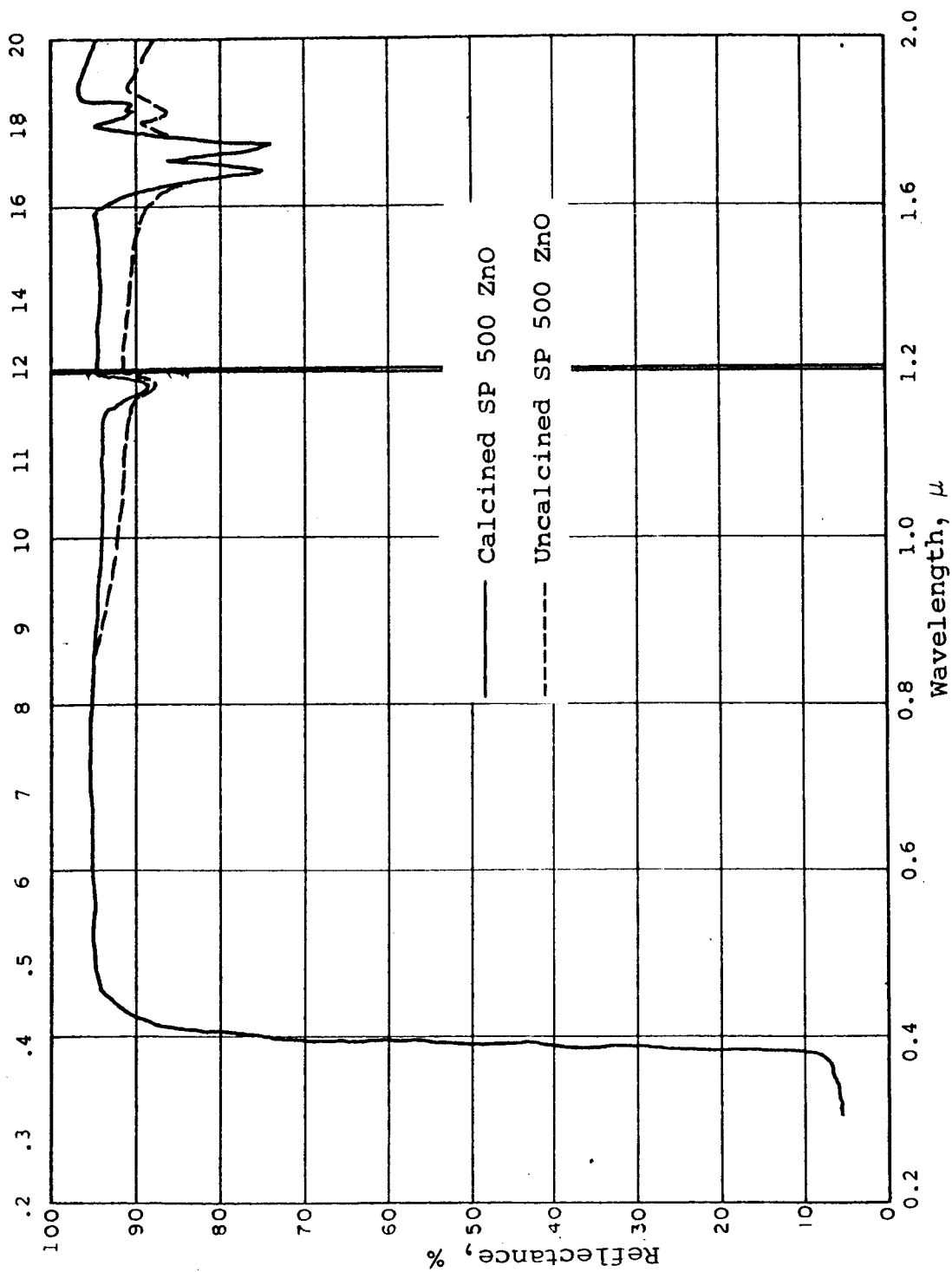
REFLECTANCE OF S-13 (Calcined SP 500)

Figure 8

Wavelength, μ

————— Calcined SP 500 ZnO

--------- Uncalcined SP 500 ZnO

Reflectance, %

confirm the value of pigment calcination for organic paints, which had been observed in rather extensive studies on the inorganic potassium silicate system.

C.   Effect of Particle Size

Solar absorptance values have been determined on a series of paints which were prepared from specific mixtures of SP 500 and XX 254 zinc oxide pigments.   The mean particle size for SP 500 is reported by the manufacturer to be 0.3μ diameter and that for the XX 254 is 1.5μ diameter.   The pertinent data are given in Table 8.   The paints were prepared at 100, 80, 50, 20 and 0% SP 500 pigment.   Except for the 0% SP 500 (100% XX 254), the films were cast with a Gardner knife at 10-mil wet-film thickness.   The dry-film thickness of the five specimens are given in Table 8, and their reflectances are shown in Figure 9.

Examination of the data shows the effect of mixing two zinc oxides of different particle-size distributions.   Although paint 5 is considerable thicker than the other paints, the effect of the mixing is most apparent in α_1.   The thickness of paint 5 also tends to mask the trend noted in solar absorptance. The effect of the larger pigment tends to be much more noticeable in the visible portion of the spectrum (which is manifested in α_1).   Examination of the curves in Figure 9 shows that paint 5, prepared entirely from the larger XX 254 pigment, possesses a more sharply defined near-infrared spectra compared to the other

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Table 8

SOLAR ABSORPTANCE AS A FUNCTION OF
PIGMENT PARTICLE SIZE

Paint No.	Percent SP 500	Percent XX 254	Thickness, mil	Solar Absorptance		
				α_1	α_2	α
1	100	0	5.3	0.10	0.11	0.21
2	80	20	6.5	0.11	0.11	0.22
3	50	50	6.8	0.12	0.11	0.23
4	20	80	6.8	0.13	0.11	0.24
5	0	100	13.0	0.13	0.11	0.24
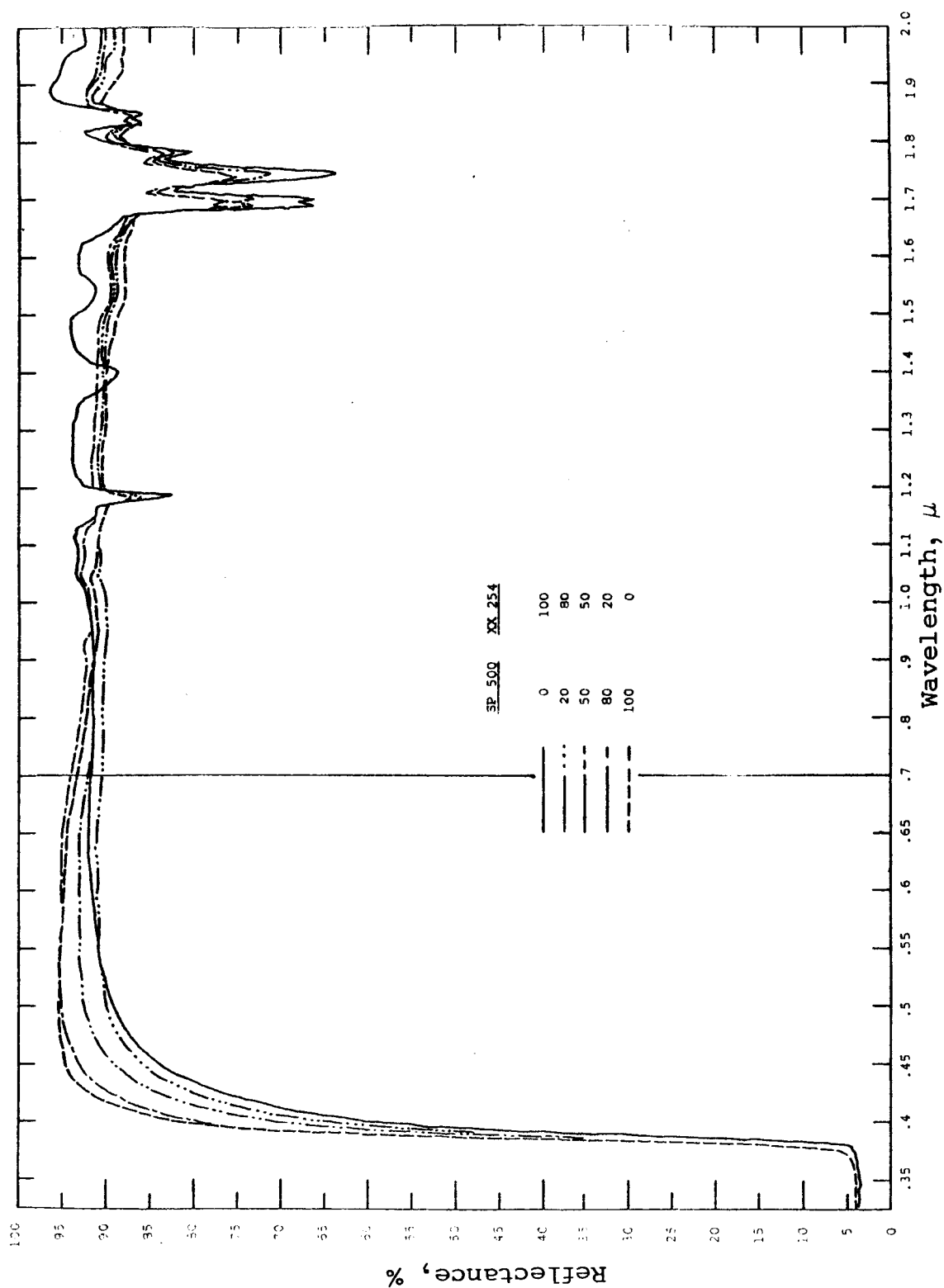
Figure 9

EFFECT OF PARTICLE SIZE ON REFLECTANCE OF
LTV-602 ZINC OXIDE PAINTS

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specimens and in this respect is analogous to the spectra observed for the microbubble coatings. This and the fact that the larger pigment causes an intensification of the vehicles absorption spectra cannot be explained at this time.

We plan to do considerably more work of this nature; we hope to be able to perform more accurate particle-size analyses during the next report period. One of the most difficult problems and one which has impaired the complete characterization of our paint films has been the inability to accurately measure both the mean particle size and the size distribution of zinc oxide pigments. We presented size analyses of various grades of zinc oxide in the last Triannual Report;[1] these analyses are admittedly in error with values of median diameter often differing from those of the manufacturer's by an order of magnitude. This is attributed to the difference in measurement technique; pigment manufactureres use both the ultraviolet-light microscope and gas absorption techniques to obtain average particle size. We require a distribution analysis for the purpose of weighting the size effects.

We have recently constructed a Kaye Disc Centrifuge [4] which is expected to greatly facilitate the particle-size analysis of our zinc oxide powders. In this technique, developed by

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[4] B. H. Kaye, British Patent No. 895,222 (1962).

Dr. B. H. Kaye[5] who recently joined IIT Research Institute, particles are centrifuged in a cylindrical transparent tank in which there is an entry port. The centrifuge is partially filled with a clear liquid, and when steady-state conditions are attained, the powder to be examined is injected as a low-concentration suspension through the entry port. A layer of suspension is formed on top of the free surface of the fluid in the tank. The particles travel outwards, and the concentration of each size is measured by means of a light beam passing through the tank at a given distance from the center of rotation. The system is essentially a photosedimentometer.

D. Degradation of Polysiloxanes

Organic materials undergo chemical changes when subjected to radiation processes. These processes can be photolytic, gamma-ray, or electron radiation. The resulting chemical and physical changes which occur as a consequence of radiation depend on the conditions of the environment surrounding the system in question, i.e., the presence or absence of oxygen, pressure, temperature, etc. In polymeric systems, the degradative changes generally will be accompanied by cross-linking (chain scission and recombination), chain scission alone, and certain oxidative changes. These result from the reaction of free radicals formed in the polymer by the radiation processes.

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[5] M. J. Groves, B. H. Kaye, and B. Scarlett, "The Size Analysis of Sub-Sieve Powders Using a Centrifugal Photosedimentometer," accepted for publication, British Chem. Eng.
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However, the reaction products can vary, as previously noted, depending on the immediate environmental conditions.

For example, free radicals, trapped in the polymer, cause color formation.[6-8] But in the presence of oxygen, Miller [9], demonstrated with election spin resonance (ESR) that irradiated polyvinyl chloride which has been exposed to air loses radicals at a much greater rate than when retained in vacuo. This loss of free radicals has been correlated with a loss of color formation which has been attributed to the formation of a peroxy radical by several investigators. [10-11] Yegorova and coworkers[12] have shown that the free-radical formation is temperature dependent, and St. Pierre and Dewhurst [13] have demonstrated the

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[6] C. A. Wall and R. E. Florin, J. Appl. Polymer Sci., 5, 251 (1959).

[7] S. Ohnishi et. al., ibid. 6, 629 (1962).

[8] A. L. Alexander, et. al. WADD TR 60-703, Part I. Nov. 1960; Part II Dec. 1960.

[9] A. A. Miller, J. Phys. Chemistry 63, 1755 (1959).

[10] A. Chapiro, J. Chim. Phys., 53, 895 (1956).

[11] B. R. Loy, J. Phys. Chem., 65, 58 (1961).

[12] Z. S. Yegorova et. al., Polymer Sci. (U.S.S.R.), 4, 23 (1963).

[13] L. E. St. Pierre, and H. A. Dewhurst, J. Chem. Phys. 29, 241, (1958).

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total inhibition of carbon-carbon cross-links by the introduction of sufficient oxygen. The latter[14] also demonstrated the oxygen termination of free radicals by the formation of a carboxylic acid and two types of peroxides during the radiolysis of hexamethyldisiloxane. The loss of color[15] in the presence of oxygen and the formation of oxidized end groups[16] have also been demonstrated in the radiation of polyamides.

In the absence of oxygen, the generated free radicals are not destroyed. Thus, the resultant reactions are mainly disproportionation, which gives rise to chain scissions and migration, giving rise to cross-links.[17,18] In addition, if the free radicals are long-lived, color formation will be observed, as noted previously. Lawton and coworkers[19] have stated that the trapping of free radicals in polymer systems occurs 1) within the crystallites of the polymers, 2) in the amorphous phase below the glass transition temperature, and 3) in the heavily cross-linked polymers where radical recombination is less possible due to shielding of or attachment to the network. More recently,

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[14] L. E. St. Pierre and H. A. Dewhurst, J. Phys. Chem., 64, 1060 (1960).

[15] J. Zimmerman, J. Appl. Polymer Sci., 2, 181 (1959)

[16] R. F. Moore, Polymer, 4, 493 (1963)

[17] J. Zimmerman, J. Polymer Sci., 46, 151 (1960).

[18] C. T. Graves and M. G. Ormerod, Polymer, 4, 81 (1963).

[19] E. J. Lawton et al, J. Poly. Sci., 32, 257 (1958)

Ormerod[20] has shown that hydrogen has a marked effect on radical decay rates in irradiated polyethylene, since free radicals can travel intra- and inter-molecularly.

Only recently has attention been turned to radiation damage in polysiloxanes. Miller[21] examined the electron irradiation of a linear polydimethylsiloxane oil in the absence of oxygen and found that both $\equiv Si \dotplus CH_3$ and $\equiv SiCH_2 \dotplus H$ scissions occurred with the evolution of H_2, CH_4 and C_2H_6 as the gaseous products and the formation of cross-links. He also observed some anomalies in the overall radiation chemical effects in the transition from the fluid to the solid state. Subsequently, Miller[22] noted the decrease in cross-linking in the presence of oxygen as a function of its pressure and concluded that these residual cross-links were not peroxide bonds. He also found that hydrogen transfer agents (e.g., mercaptans) retarded cross-linking and that scission of the siloxane backbone was negligible in comparison with the cross-linking reaction.

More recently, Ormerod and Charlesby[23] examined the effect of irradiation on linear dimethylsiloxane in the absence of oxygen. They also found a temperature-linked anomaly in the

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[20]M. G. Ormerod, Polymer, 4, 451 (1963).

[21]A. A. Miller, J. Am. Chem. Soc., 82, 3519 (1960).

[22]A. A. Miller, ibid, 83, 31 (1961).

[23]M. G. Ormerod and A. Charlesby, Polymer, 4, 459 (1963).

cross-linking reaction and concluded that the radiation chemistry

differed between the solid and liquid states. They believe that an

ionic cross-linking mechanism might be possible at low temperatures,

although a free-radical mechanism appears to predominate at room

temperature where radicals are difficult to detect because of

rapid reactions. As further confirmation of the two temperature-

dependent mechanisms, they reported that stable free radicals

could be produced in a vinyl-containing polysiloxane at room

temperature, but not at low temperature.

In this respect, the polydimethylsiloxane polymer system

should be inherently stable to ultraviolet radiation in the

2000- to 4000-A wavelength region. This is attributed to the

fact that the silicone-oxygen backbone does not absorb radiation

of wavelengths longer than about 3900 A, and the methyl side

groups (on the silicone atoms) do not abosrb appreciably at wave-

lengths greater than about 1400 A. One wonders therefore why

the purely methyl silicone polymers are not even more stable to

ultraviolet radiation in vacuum, especially since our laboratory's

simulated solar environment contains no ultraviolet of wave-

lenths shorter than about 2100 A. This consideration prompted

us to examine the influence of residual aromatic contamination

in our methyl silicone polymers, This contamination could re-

sult from occluded, aromatic solvents (we use tolune and xylene

as silicone solvents) as well as the catalysts used to cure the

resins.

We accordingly prepared the basic S-13 formulation both at

reduced catalyst levels and entirely with aliphatic solvents.

The results of space simulation on the modified specimens is shown in Table 9. It will be noted that decreasing the catalyst concentration by one-half appeared to increase the stability. In addition, the use of butyl alcohol as the solvent for S-13 resulted in one of the smallest $\Delta \alpha$'s ever observed for a 2000-ESH test.

Table 9

EFFECT OF CONTAMINATION ON THE STABILITY
OF THE S-13 ZINC OXIDE-LTV 602 THERMAL-CONTROL PAINT

Catalyst Concentration drops/35 g	Solvent	Exposure		Solar Absorptance	
		ESH	Solar Factor	α	$\Delta \alpha$
2	Toluene	0	–	0.230	–
		2000	10.7	0.262	0.032
1	Toluene	0	–	0.188	–
		2000	10.0	0.205	0.017
1	Carbon tetrachloride	0	–	0.208	–
		2000	10.0	0.219	0.011
1	Butyl alcohol	0	–	0.194	–
		2000	10.0	0.197	0.003

These experiments indicate the importance of polymer purity in achieving stability to ultraviolet radiation in vacuum. Although we are unable at this time to define the mechanisms associated with these observations, Dr. S. Siegel[24] has suggested

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[24] Dr. S. Siegel, Aerospace Corporation, Private communication.

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that the presence of occluded aromatic solvent molecules might behave as energy sinks which subsequently transfer their energy to the polymer molecule. He commented further that the commercial silicone material which we use (LTV-602) could contain traces of aromatic contaminants remaining from the polymerization process.

Thus, it would appear that the radiation chemistry of the polysiloxanes -- especially under ultraviolet radiation in vacuum -- needs further elucidation. We therefore have initiated a survey of the literature pertaining to the radiation chemistry and photolysis of polydimethylsiloxanes (and methyl-phenyl silicones as well) and the photolysis in vacuum of polymers in general. A research program being planned will attempt to elucidate the mechanisms associated with the degradation of polydimethylsiloxanes by ultraviolet irradiation in vacuum. Auxiliary equipment is being designed and constructed for the irradiation of polydimethylsiloxane films both at liquid nitrogen and room temperature with provisions for ESR determination and the determination of outgassed products by mass spectrometry. The possible contribution of attenuated total reflectance (ATR) as a means of determining the changes in polymer structure will be investigated.